

# Revealing the mechanisms of NH<sub>3</sub> adsorption and reactions in catalytic NO<sub>x</sub> reduction over Cu<sub>x</sub>/CHA zeolites by in situ DRIFTS spectroscopy

Yali Shen<sup>a</sup>, Zhiqiang Wang<sup>b</sup>, Shasha Ge<sup>a</sup>, Li Wang<sup>a</sup>, Wangcheng Zhan<sup>a</sup>, Qiguang Dai<sup>a</sup>,  
Yanlong Guo<sup>a</sup>, Yun Guo<sup>a,\*</sup>, Aiyong Wang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, PR China

<sup>b</sup> State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, PR China

## ARTICLE INFO

### Keywords:

NH<sub>3</sub>-SCR

Cu-SSZ-13

NH<sub>3</sub> solvation

Intra-zeolite oxolation

## ABSTRACT

Adsorption and activation of NH<sub>3</sub> on Cu-SSZ-13 were essential for NO<sub>x</sub> removal, however, their important role at the molecular level remains unclear. In this work, the Al-rich Cu/SSZ-13 (Cu<sub>x</sub>/CHA) catalysts were synthesized by the incipient-wetness impregnation method, and the NH<sub>3</sub>-SCR performance was investigated. It is found that high Cu content promoted the formation of Z-[Cu(OH)]<sup>+</sup> and CuO<sub>x</sub> particles, enhanced the adsorption capacity of NO<sub>x</sub>, and increased the intra-zeolite oxolation process in the Cu<sub>x</sub>/CHA catalysts. *In situ* DRIFTS results showed that the Z-[Cu(OH)(NH<sub>3</sub>)<sub>x</sub>]<sup>+</sup> (x < 3) exhibited analogous properties to B-NH<sub>4</sub><sup>+</sup>, but it would convert to Z-[Cu(OH)(NH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> with increasing NH<sub>3</sub> adsorption time and exhibit L-NH<sub>3</sub> properties. Those findings could provide a new insight into understanding the adsorption and activation of NH<sub>3</sub> in low-temperature reactions, as well as new ideas for improving NO<sub>x</sub> conversion during cold start.

## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) are characteristic pollutants of diesel vehicle exhaust emissions, and NH<sub>3</sub> selective catalytic reduction (NH<sub>3</sub>-SCR) has been recognized as the most widely used and effective method for NO<sub>x</sub> emission control [1,2]. Recently, small-pore Cu-SSZ-13 catalyst, with CHA structure, have excellent NH<sub>3</sub>-SCR catalytic performance in the range of 200–450 °C and have been widely investigated as mainstream NH<sub>3</sub>-SCR catalysts [3–5]. However, the low performance below 200 °C does not ensure effective NO<sub>x</sub> removal under cold-start conditions [6]. Therefore, studies on the NO<sub>x</sub> reduction mechanism of Cu-SSZ-13 catalysts provide theoretical support for better understanding and design of catalysts with excellent low-temperature NH<sub>3</sub>-SCR catalytic performance.

Isolated Cu<sup>II</sup> ions and CuO<sub>x</sub> are the main forms of Cu species existed in Cu-SSZ-13, in which two types of isolated Cu<sup>II</sup> ions exist, one is Z<sub>2</sub>-Cu<sup>2+</sup> located in the double 6-membered ring position (Z represents the framework Al), and the other is Z-[Cu(OH)]<sup>+</sup> located in the 8-membered ring position [7–9]. In earlier studies, it was suggested that Z-[Cu(OH)]<sup>+</sup> occurred only when Z<sub>2</sub>-Cu<sup>2+</sup> was fully saturated because Z<sub>2</sub>-Cu<sup>2+</sup> was

thermodynamically more stable than Z-[Cu(OH)]<sup>+</sup> [10,11]. With further research, Z-[Cu(OH)]<sup>+</sup> was found to be formed along with Z<sub>2</sub>-Cu<sup>2+</sup> due to kinetic stabilization effects during the ion exchange process [12]. Furthermore, the synthesis method [13], Cu content [14], and Si/Al ratio [14] of the zeolite will affect the distribution of Cu species (i.e., Z-[Cu(OH)]<sup>+</sup>, Z<sub>2</sub>-Cu<sup>2+</sup>, and CuO<sub>x</sub>) in Cu-SSZ-13.

In the case of the standard SCR reaction on Cu-SSZ-13 zeolite, active site evolution consists mainly of two half-cycle reactions, i.e., reduction cycle (Cu<sup>2+</sup> → Cu<sup>+</sup>) and oxidation cycle (Cu<sup>+</sup> → Cu<sup>2+</sup>) [9,15–17]. It has been found that the NH<sub>3</sub>-SCR reaction exhibited different reaction mechanisms in the lower and higher temperature regions [18]. The active site in the lower temperature range is dynamically changing and dominated by transient Cu dimer formed by NH<sub>3</sub>-dissolved [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> species [19–21], whereas the active site in the high-temperature region is an isolated Cu<sup>II</sup> ionic site [18]. In addition, the researcher also found that Z-[Cu(OH)]<sup>+</sup> exhibited higher activity than Z<sub>2</sub>-Cu<sup>2+</sup> in both reduction by NH<sub>3</sub> and oxidation to bidentate nitrate by NO [22]. Lee et al. [23] found that Z-[Cu(OH)]<sup>+</sup> species had higher mobility and were more readily diffusible than the Z<sub>2</sub>-Cu<sup>2+</sup> species during the forming of the dimerized Cu intermediates (i.e.,

\* Corresponding authors.

E-mail addresses: [yunguo@ecust.edu.cn](mailto:yunguo@ecust.edu.cn) (Y. Guo), [wangaiyong@ecust.edu.cn](mailto:wangaiyong@ecust.edu.cn) (A. Wang).

<https://doi.org/10.1016/j.apcatb.2024.124094>

Received 8 March 2024; Received in revised form 7 April 2024; Accepted 18 April 2024

Available online 19 April 2024

0926-3373/© 2024 Elsevier B.V. All rights reserved.

$[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+ - \text{O}_2 - [\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$ ), resulting in higher reactivity properties. Thus, the  $\text{NH}_3$ -SCR activity in the low-temperature region correlated mainly with  $\text{Z} - [\text{Cu}(\text{OH})]^+$  species after  $\text{NH}_3$  solvation.

The  $\text{NH}_3$  solvation process was very important for the low-temperature  $\text{NH}_3$ -SCR performance. It has been shown that the existence of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  affected the coordinating environment of Cu species in Cu-SSZ-13 catalyst at temperatures below  $250^\circ\text{C}$  [9]. In the existence of  $\text{H}_2\text{O}$ , Cu species form hydrated Cu complexes, whereas when  $\text{NH}_3$  was present,  $\text{NH}_3$  preferentially adsorbs Cu species within the Cu-SSZ-13 zeolites to form mobile Cu-amine complexes, leading to higher mobility [9,24]. For isolated  $\text{Cu}^{\text{II}}$  ions on Cu-SSZ-13 ( $\text{Z}_2 - \text{Cu}^{2+}$  and  $\text{Z} - [\text{Cu}(\text{OH})]^+$ ), with introducing  $\text{NH}_3$  species, it is possible to generate  $\text{Z}_2 - [\text{Cu}(\text{NH}_3)_2]^{2+}$ ,  $\text{Z}_2 - [\text{Cu}(\text{NH}_3)_3]^{2+}$ ,  $\text{Z}_2 - [\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $\text{Z} - [\text{Cu}(\text{OH})(\text{NH}_3)]^+$ ,  $\text{Z} - [\text{Cu}(\text{OH})(\text{NH}_3)_2]^+$ , and  $\text{Z} - [\text{Cu}(\text{OH})(\text{NH}_3)_3]^+$  species [1,22,24,25]. In fact, the generation of Cu-amine complexes weakened the interaction between isolated  $\text{Cu}^{\text{II}}$  ions and the zeolite framework and increased the mobility of isolated  $\text{Cu}^{\text{II}}$  ions, which allowed the  $\text{NH}_3$ -solvated Cu ions to form Cu dimers inside or across the zeolite cage, and thus to be involved in the  $\text{NH}_3$ -SCR catalytic reactions in the low-temperature region. However, theoretical calculations suggested that linear  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  was more mobile, but as noted above, no change in valence of the isolated  $\text{Cu}^{\text{II}}$  ions was observed during  $\text{NH}_3$  solvation process, thus requiring reaction with NO to generate linear  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  species, which in turn reacts with  $\text{O}_2$  to generate  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+ - \text{O}_2 - [\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  intermediates [26].

Moreover, there was controversy over the number of  $\text{NH}_3$  coordination sites for the isolated  $\text{Cu}^{\text{II}}$  ion on Cu-SSZ-13, with some scholars suggesting that the  $\text{Z}_2 - \text{Cu}^{2+}$  site was coordinated to a maximum of two  $\text{NH}_3$ , whereas the  $\text{Z} - [\text{Cu}(\text{OH})]^+$  site was coordinated to a maximum of one  $\text{NH}_3$  [19]. In contrast, some scholars suggested that isolated  $\text{Cu}^{\text{I}}$  ions would dissolve with two  $\text{NH}_3$  ligands to form linear  $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ , while the isolated  $\text{Cu}^{\text{II}}$  ion would form a four-coordination complex with four or three  $\text{NH}_3$ , i.e.,  $\text{Z}_2 - [\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $\text{Z} - [\text{Cu}(\text{OH})(\text{NH}_3)_3]^+$  [8,18]. Although the  $\text{NH}_3$  solvation process of Cu species on Cu-SSZ-13 has been investigated, however, the relevant properties exhibited by the  $\text{NH}_3$  solvation process need to be further investigated.

In this paper, a series of aluminum-rich  $\text{Cu}_x/\text{SSZ-13}$  ( $\text{Cu}_x/\text{CHA}$ ) were prepared by using the incipient-wetness impregnation technique. The relationship between  $\text{Cu}^{2+}$  sites and reaction performance in  $\text{Cu}_x/\text{CHA}$  was also established by combining XRD Rietveld refinement, structural characterization, redox property characterization and *in situ* spectroscopic analysis. In addition, the  $\text{NH}_3$  solvation process and reaction mechanism on  $\text{Cu}_x/\text{CHA}$  with different contents of  $\text{Z}_2 - \text{Cu}^{2+}$ ,  $\text{Z} - [\text{Cu}(\text{OH})]^+$  and  $\text{CuO}_x$  species were investigated by *in situ* DRIFTS.

## 2. Experimental

### 2.1. Catalysts preparation

Cu-SSZ-13 catalysts with different Cu content were synthesized by incipient-wetness impregnation (IWI) from commercially available H-SSZ-13 zeolites. Briefly, the needed dosage of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was first diluted with  $\text{H}_2\text{O}$  and then mixed with 2 g H-SSZ-13, ultrasonicated for 20 min, dried overnight at  $110^\circ\text{C}$ , followed by calcination for 4 h at  $550^\circ\text{C}$  in static air. The resulting powder was expressed as  $\text{Cu}_x/\text{CHA}$ , in which x is the actual copper content in the catalyst obtained by ICP-OES.

### 2.2. Characterization

The species, location and distribution properties of Cu species in  $\text{Cu}_x/\text{CHA}$  were investigated by various characterization methods, such as ICP-OES,  $\text{N}_2$  adsorption-desorption analysis, XRD, HAADF-STEM,  $\text{H}_2$ -TPR, UV-vis,  $\text{NO}_x$ -TPD, and  $\text{NH}_3$ -TPD, the specific test conditions were the same as in previous studies [27,28], see Supporting information.

The  $\text{NH}_3$  solvation process and reaction mechanism on  $\text{Cu}_x/\text{CHA}$  were investigated by *in situ* DRIFTS (Nicolet Nexus 6700 FT-IR

spectrometer), as described in the Supporting information.

### 2.3. Catalytic performance

A  $\text{NO}_x$  chemiluminescence analyzer (Thermo Fisher Model 42i-HL) and a Nicolet 6700 FT-IR spectrometer were used to investigate the NO conversion,  $\text{N}_2$  selectivity and  $\text{N}_2\text{O}$  concentration of  $\text{Cu}_x/\text{CHA}$ . The feed gas contained 500 ppm  $\text{NH}_3$ , 500 ppm NO, 5 vol%  $\text{O}_2$ , 5 vol%  $\text{H}_2\text{O}$ , and was equilibrated with Ar at a weight hourly space velocity (WHSV) of  $180,000\text{ mL}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ . Tests details on the  $\text{NH}_3$ -SCR activity and kinetics of  $\text{Cu}_x/\text{CHA}$  were given in the Supporting information.

## 3. Results and discussion

### 3.1. Structural properties

#### 3.1.1. XRD

The XRD spectra of  $\text{Cu}_x/\text{CHA}$  are presented in Fig. 1(a) and S1, all samples showed a typical CHA framework structure. No diffraction peaks of Cu-related species (such as CuO (PDF# 48-1548),  $\text{CuAl}_2\text{O}_4$  (PDF# 33-0448), and  $\text{CuAlO}_2$  (PDF# 35-1401)) were observed on  $\text{Cu}_x/\text{CHA}$ , suggesting that the Cu species were dispersed highly in SSZ-13, or the particles size was smaller than the XRD limit of detection [27]. Moreover, the ratio of the peak intensity of (101) and (211) ( $I_{(101)}/I_{(211)}$ ) was decreased with the increase of Cu content (Fig. 1(b)). The decreased  $I_{(101)}/I_{(211)}$  could correspond to the Cu species in  $\text{Cu}_x/\text{CHA}$ , the existence of which in the 8-membered ring ( $\text{Z} - [\text{Cu}(\text{OH})]^+$ ) caused a certain amount of deformation of the zeolite framework structure, thus reducing the reflectivity of the (101) crystal surface [29]. Therefore, the higher the copper content, the more  $\text{Z} - [\text{Cu}(\text{OH})]^+$  species close to the position of the 8-membered ring, and the more pronounced the resulting deformation.

The Rietveld refinement of H-SSZ-13(CHA) was first performed, and the result is shown in Figs. S1(a) and S2. As shown in Fig. S2, H-SSZ-13 (CHA) had a typical CHA structure, which mainly consisted of the 8-membered ring (8MR), 6-membered ring (6MR), and 4-membered ring (4MR) structures. Then, the Rietveld refinement of copper-containing zeolites ( $\text{Cu}_x/\text{CHA}$ ) was carried out by using the refined H-SSZ-13 structure as the initial model as in previous studies [27], and the results are illustrated in Fig. 1(d) and S1(b-e).

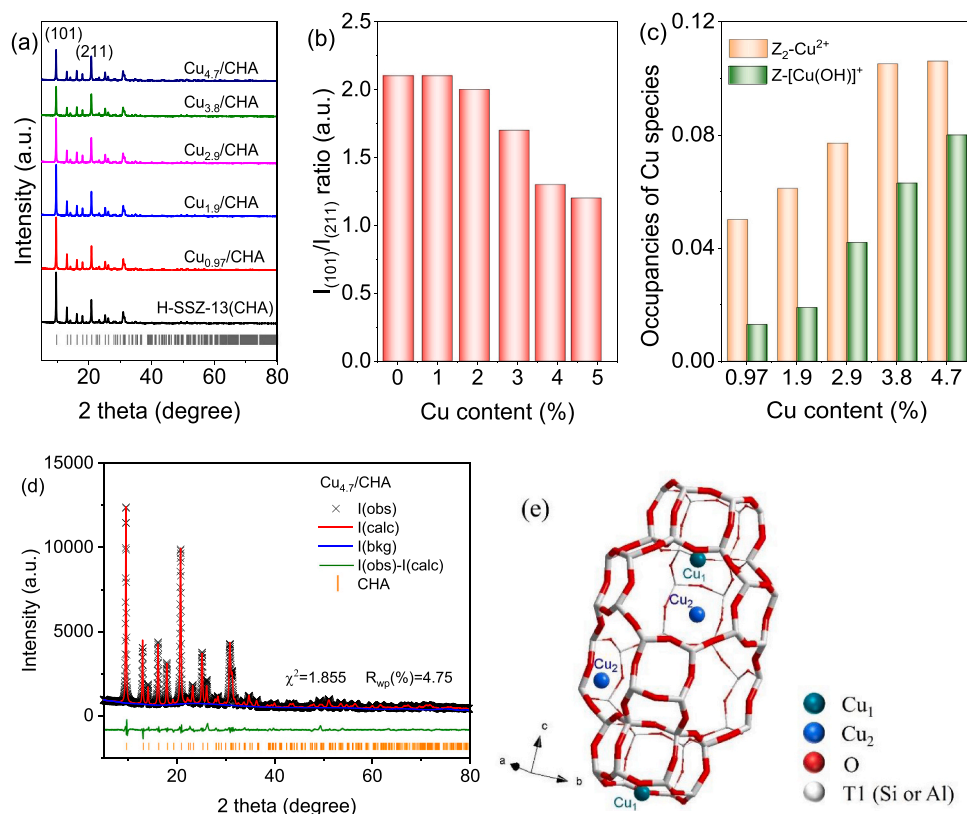
The positions of  $\text{Cu}_1$  (located in 6MR, coordinated to three oxygen atoms of the 6MRs, named as  $\text{Z}_2 - \text{Cu}^{2+}$ ) and  $\text{Cu}_2$  (located in the chabazite cage nearby 8MR, named as  $\text{Z} - [\text{Cu}(\text{OH})]^+$ ) in  $\text{Cu}_x/\text{CHA}$  are illustrated in Fig. 1(e). As demonstrated in Table S1 and Fig. 1(c), with increasing Cu content, the  $\text{OCC}_{\text{Cu1}}$  (the occupancies of  $\text{Cu}_1$ ) in  $\text{Cu}_x/\text{CHA}$  increased significantly firstly and then slightly changed when the Cu content was higher than 3.8 wt%. At the same time, the  $\text{OCC}_{\text{Cu2}}$  (occupancies of  $\text{Cu}_2$ ) in  $\text{Cu}_x/\text{CHA}$  increased monotonically with increasing Cu content. These results suggested that more Cu species occupied the ion-exchange sites of zeolites as increasing Cu content and that  $\text{Z}_2 - \text{Cu}^{2+}$  could be saturated when the copper content was higher than 3.8 wt%.

#### 3.1.2. $\text{N}_2$ adsorption-desorption analysis

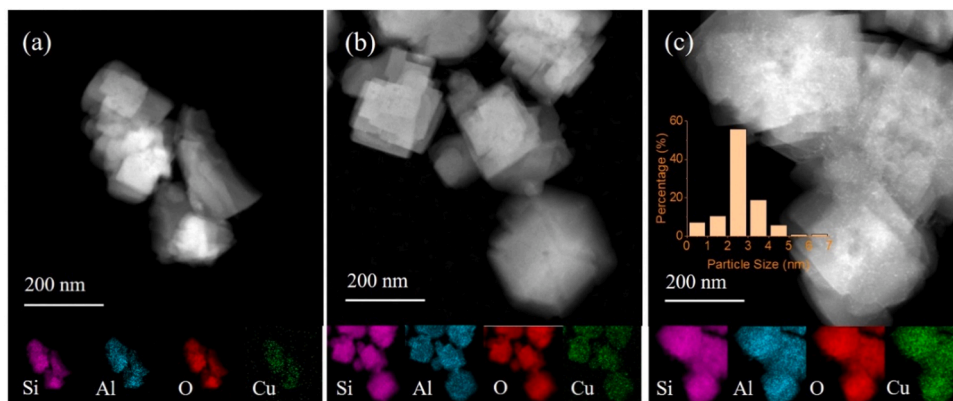
BET surface areas ( $S_{\text{BET}}$ ) and pore volumes ( $V_{\text{pore}}$ ) of  $\text{Cu}_x/\text{CHA}$  are summarized in Table S2 and Fig. S3. The  $S_{\text{BET}}$  and  $V_{\text{pore}}$  of  $\text{Cu}_x/\text{CHA}$  decreased with increasing copper content, which could be due to the blocking of zeolite pores by Cu ions entering into the pores, thus decreasing the  $S_{\text{BET}}$  and  $V_{\text{pore}}$  of  $\text{Cu}_x/\text{CHA}$ , and the higher the Cu content, the more significant the effect.

#### 3.1.3. STEM and EDS

The structure and elemental distribution of  $\text{Cu}_x/\text{CHA}$  were carried out by HAADF-STEM and EDS mapping (Fig. 2). For  $\text{Cu}_{0.97}/\text{CHA}$ , Cu was highly dispersed (Fig. 2(a)). More Cu was found in  $\text{Cu}_{1.9}/\text{CHA}$  (Fig. 2(b)) and highly dispersed. Further increasing the Cu content to 4.7 wt%, most of the copper was highly dispersed in the  $\text{Cu}_{4.7}/\text{CHA}$  zeolite,



**Fig. 1.** (a) XRD patterns of  $\text{Cu}_x/\text{CHA}$  catalyst; (b) The ratio of  $I_{(101)}/I_{(211)}$  obtained by (a); (c) The occupancies of Cu species; (d) XRD pattern and calculated Rietveld refinement pattern of  $\text{Cu}_{4.7}/\text{CHA}$ . (e) Structural models of  $\text{Cu}_x/\text{CHA}$  samples. ( $\text{Cu}_1$ : located in 6MR, coordinated to three oxygen atoms of the 6MRs, such as  $\text{Z}_2\text{-Cu}^{2+}$ ;  $\text{Cu}_2$ : located in the chabazite cage, such as  $\text{Z}[\text{Cu}(\text{OH})]^{+}$  in 8MR).



**Fig. 2.** STEM-EDS mappings of (a)  $\text{Cu}_{0.97}/\text{CHA}$ , (b)  $\text{Cu}_{1.9}/\text{CHA}$ , (c)  $\text{Cu}_{4.7}/\text{CHA}$ .

however, a small amount of copper was present as  $\text{CuO}_x$  particles with a mean particle diameter of 2.3 nm, as shown as Fig. 3(c). Those results indicated that low contents could be well dispersed in the zeolite, while Cu species could agglomerate to produce  $\text{CuO}_x$  species when the copper content was too high.

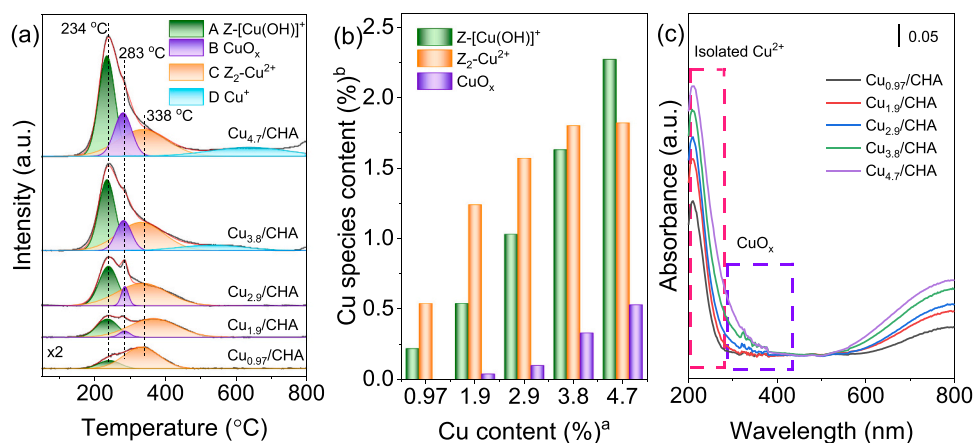
### 3.2. Distribution of different Cu species

#### 3.2.1. $\text{H}_2$ -TPR

The reducible properties of  $\text{Cu}_x/\text{CHA}$  were further investigated by  $\text{H}_2$ -TPR testing as illustrated in Fig. 3 and S4. Of note, there was no  $\text{H}_2$  consuming peak observed in H-SSZ-13(CHA) (Fig. S4), demonstrated that all the  $\text{H}_2$  consuming peaks in the  $\text{H}_2$ -TPR curves of  $\text{Cu}_x/\text{CHA}$  originated from the Cu species reduction. The  $\text{H}_2$  consuming peaks of

$\text{Cu}_x/\text{CHA}$  (Fig. 3) could be decomposed into four peaks (A, B, C, and D). Peak B ( $283^\circ\text{C}$ ) was ascribed to the reduction of  $\text{CuO}_x$  particles ( $\text{Cu}^{2+} \rightarrow \text{Cu}^0$ ) [27]. Peak A ( $234^\circ\text{C}$ ) and peak C ( $338^\circ\text{C}$ ) were attributed to the reduction of isolated  $\text{Cu}^{2+}$  ions ( $\text{Z}[\text{Cu}(\text{OH})]^{+}$  and  $\text{Z}_2\text{-Cu}^{2+}$ ) to isolated  $\text{Cu}^{+}$  ions, respectively [30,31]. And peak D ( $> 500^\circ\text{C}$ ) was assigned to the further reduction of isolated  $\text{Cu}^{+}$  ( $\text{Cu}^{+} \rightarrow \text{Cu}^0$ ) [32].

The contents of different Cu species in the  $\text{Cu}_x/\text{CHA}$  catalysts were calculated according to  $\text{H}_2$ -TPR, and summarized in Fig. 3(b) and S5. Fig. 3(b) showed that the amount of  $\text{Z}[\text{Cu}(\text{OH})]^{+}$  and  $\text{CuO}_x$  (calculated by  $\text{H}_2$ -TPR) in the  $\text{Cu}_x/\text{CHA}$  increased remarkably with the increase of Cu content (obtained by ICP-OES). However, the amount of  $\text{Z}_2\text{-Cu}^{2+}$  in the  $\text{Cu}_x/\text{CHA}$  increased remarkably with the increase of Cu content from 0.97 wt% to 3.8 wt%, but did not change significantly when the copper content was higher than 3.8 wt%. Those results were also verified in the



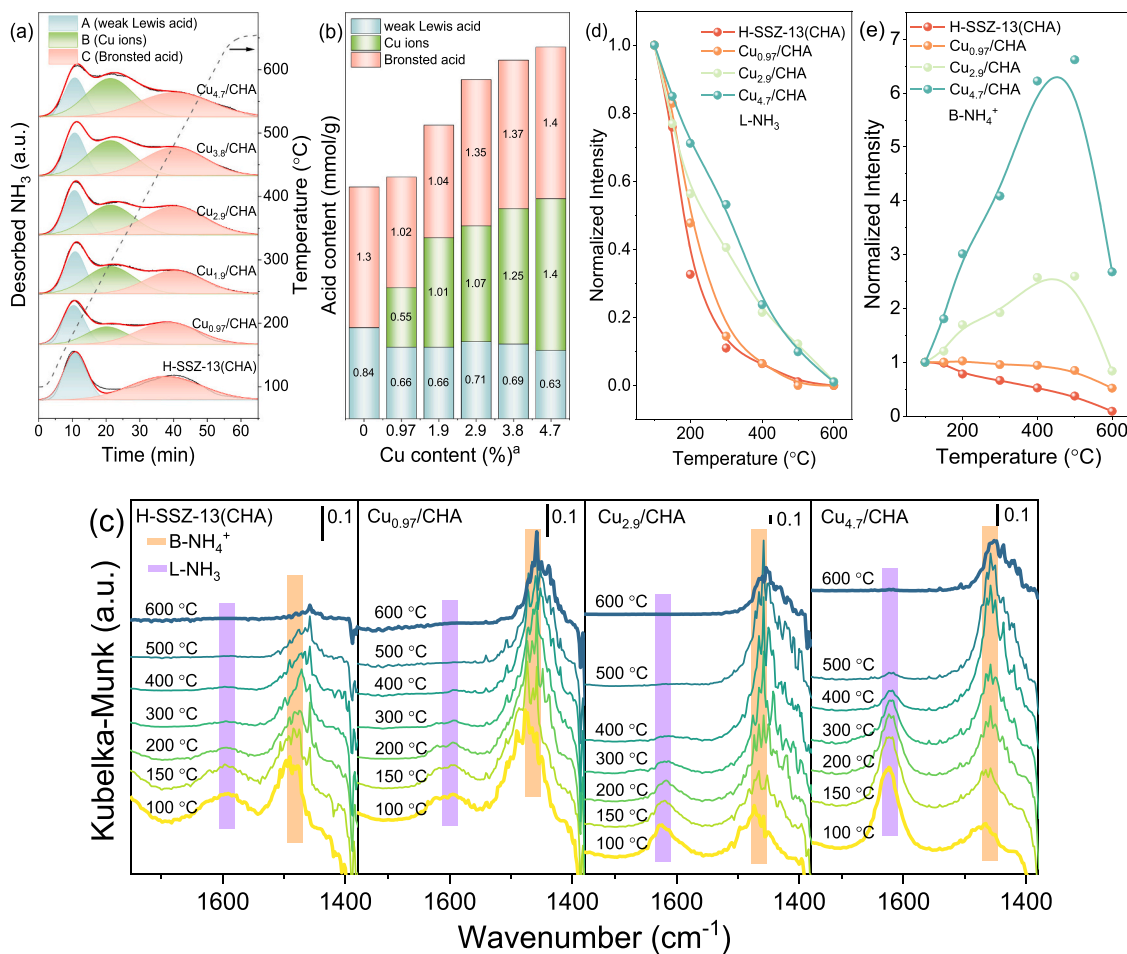
**Fig. 3.** (a) H<sub>2</sub>-TPR profiles of Cu<sub>x</sub>/CHA catalysts, and their deconvoluted results (b) of Cu<sub>x</sub>/CHA catalysts; (c) UV-vis spectroscopy of Cu<sub>x</sub>/CHA catalysts. <sup>a</sup>: Obtained by ICP-OES. <sup>b</sup>: Calculated from hydrogen consumption peaks below 500 °C.

results of XRD Rietveld refinement and HAADF-STEM, which was probably resulted from the limited amount of 6MR sites in the CHA zeolite, leading to an easier generation of CuO<sub>x</sub> and Z-[Cu(OH)]<sup>+</sup> species at high Cu contents. In addition, Fig. S5 showed that the Z<sub>2</sub>-Cu<sup>2+</sup> species percentage decreased with increasing Cu content, while the CuO<sub>x</sub> and Z-[Cu(OH)]<sup>+</sup> species percentage increased. These results suggested that

high Cu content promoted the formation of Z-[Cu(OH)]<sup>+</sup> and CuO<sub>x</sub> particles.

### 3.2.2. UV-vis

UV-vis spectroscopy further examined the existence status of Cu species on Cu<sub>x</sub>/CHA. According to previous reports, the band at



**Fig. 4.** (a) The NH<sub>3</sub>-TPD profiles of H-SSZ-13(CHA) and Cu<sub>x</sub>/CHA samples; (b) The acid content of samples obtained by the peak fitting of the results in (a); (c) In situ DRIFTS spectra of Cu<sub>x</sub>/CHA during desorption processes, and plot of the intensity of the Lewis acid (d) and Brønsted acid (e) bands on Cu<sub>x</sub>/CHA as a function of purge temperature after normalization. (Cu<sub>x</sub>/CHA were pretreated in a flow of 1000 ppm NH<sub>3</sub> at 100 °C and then purged with Ar at different temperatures; <sup>a</sup>: Obtained by ICP-OES).



~210 nm was connected to oxygen-to-metal charge transfer, which related to the isolated  $\text{Cu}^{2+}$  cations (i.e.,  $\text{Z}[\text{Cu}(\text{OH})]^+$  and  $\text{Z}_2\text{-Cu}^{2+}$ ) stabilized in the framework [33,34]. The bands at around 250 nm was related to the charge transfer of Cu in dimeric  $\text{CuO}_x$  cluster, and 340 nm was connected to the charge transfer of Cu in crystalline  $\text{CuO}_x$  [35]. There was a broad band at around 785 nm that resulted from the d-d transition of oxygen-generated electrons from  $\text{Cu}^{2+}$  in the out-of-framework  $\text{CuO}_x$  particles around the twisted octahedron [34, 36].

As shown in Fig. 3(c), for the low Cu content sample (i.e.,  $\text{Cu}_{0.97}/\text{CHA}$ ), Cu species exist primarily in the form of isolated  $\text{Cu}^{2+}$  cations in the CHA framework. Moreover, increasing the Cu loadings could increase the bands associated with isolated  $\text{Cu}^{2+}$  cations and  $\text{CuO}_x$  species [37], which were consistent with the results of TPR. After normalization (Fig. S6), the bands associated with  $\text{CuO}_x$  gradually increased with increasing copper content, indicating that higher copper content was favorable for  $\text{CuO}_x$  species generation, as confirmed in  $\text{H}_2$ -TPR and STEM.

### 3.3. Surface adsorption properties of Catalysts

#### 3.3.1. $\text{NH}_3$ -TPD

The acidic property played a crucial role in the  $\text{NH}_3$ -SCR reaction on the Cu zeolites, the effects of Cu content on the acidity of  $\text{Cu}_x/\text{CHA}$  were investigated by  $\text{NH}_3$ -TPD, and shown in Fig. 4. Two distinct desorption peaks were observed on the resolved curve of H-SSZ-13(CHA), in addition, a new desorption peak (250–350 °C) was found with the introduction of Cu. According to the available studies on  $\text{NH}_3$  adsorption on Cu-SSZ-13 zeolite, the peak A at low-temperature (~190 °C) was considered to be a weakly adsorbed  $\text{NH}_3$  species, which were produced by surface OH groups and extra-framework Al [28,38]. The mid-temperature peak B (250–350 °C) was due to  $\text{NH}_3$  adsorption onto the strong Lewis acid sites, which were formed by the isolated  $\text{Cu}^{2+}$  ions at ion-exchanged sites [39]. The peak C at high-temperature (~500 °C) was ascribed to  $\text{NH}_3$  adsorption onto the strong Brønsted acid sites [28, 39].

Furthermore, the amount of acid in each desorption peak was calculated by peak area, as shown in Fig. 4(b). For the Cu-containing zeolites ( $\text{Cu}_x/\text{CHA}$ ), the acid amount corresponding to B peaks increased with increasing Cu content. The  $n(\text{NH}_3)/n(\text{Cu})$  ratios were further calculated from the B peak of  $\text{NH}_3$ -TPD and the ICP-OES results, which are shown in Table S2. The  $n(\text{NH}_3)/n(\text{Cu})$  ratio in  $\text{Cu}_{0.97}/\text{CHA}$  was 3.6, in the range of 3–4, which is probably due to the fact that the Cu species in  $\text{Cu}_{0.97}/\text{CHA}$  were present in the form of  $\text{Z}[\text{Cu}(\text{OH})]^+$  and  $\text{Z}_2\text{-Cu}^{2+}$ . These two copper species could form a four-coordination complexes with three or four  $\text{NH}_3$ , respectively. It was noteworthy that the  $n(\text{NH}_3)/n(\text{Cu})$  ratio decreased with increasing Cu content. Combined with the  $\text{H}_2$ -TPR results, it might be attributed to the increase in  $\text{Z}[\text{Cu}(\text{OH})]^+$  and  $\text{CuO}_x$  content in the  $\text{Cu}_x/\text{CHA}$  catalysts with increasing copper content. In addition, compared to H-SSZ-13(CHA), the peak C decreased significantly from 1.3 to 1.02 mmol/g in  $\text{Cu}_{0.97}/\text{CHA}$ , indicating that Cu could be in the ion-exchange site, thereby reducing the amount of the Brønsted acid site. In general, the number of Brønsted acid sites in zeolite decreased as the level of ion exchange increased. Combined with the result in Fig. 3, the number of Brønsted acid sites in  $\text{Cu}_x/\text{CHA}$  should decrease with increasing Cu content. However, as the Cu content increased from 0.97 wt% to 4.7 wt%, the acid content of the C peak increased from 1.02 mmol/g to 1.4 mmol/g, which indicated that there might be other reasons for the increase of C peaks.

Moreover, the desorption processes of adsorbed  $\text{NH}_3$  species on H-SSZ-13(CHA) and  $\text{Cu}_x/\text{CHA}$  were further examined by *in situ* DRIFTS spectra and are illustrated in Fig. 4(c) and S7. As can be seen, the negative bands at 3800–3500  $\text{cm}^{-1}$  were originated from the stretching vibrations of the O-H bonds which consumed by the adsorption of  $\text{NH}_3$  [11]. The bands at 3100–3400  $\text{cm}^{-1}$  and 1400–1700  $\text{cm}^{-1}$  were related to the stretching vibrations and bending vibrations of N-H in adsorbed

$\text{NH}_3$  species, respectively [27]. The bands at 1457–1491  $\text{cm}^{-1}$  correspond to the bending vibrations of N-H in  $\text{NH}_4^+$ , which adsorbed on the Brønsted acid sites ( $\text{B-NH}_4^+$ ) [28]. Whereas, the bands at 1585–1621  $\text{cm}^{-1}$  were derived from the bending vibrations of N-H in the  $\text{NH}_3$  which coordinated to the Lewis acid sites ( $\text{L-NH}_3$ ) [27,28].

Fig. 4(d) and (e) plots the variation of the  $\text{NH}_3$  adsorbed on the Lewis and Brønsted sites with temperature, respectively. For the Cu-free zeolite, both  $\text{L-NH}_3$  and  $\text{B-NH}_4^+$  decreased with increasing purging temperature. In contrast, the Cu-containing zeolites ( $\text{Cu}_x/\text{CHA}$ ) exhibited different trends, that is,  $\text{L-NH}_3$  monotonically decreased with increasing temperature (Fig. 4(d)), while  $\text{B-NH}_4^+$  first increased and then decreased (Fig. 4(e)). These results demonstrated that an oxolation process (i.e.  $\text{Z}[\text{Cu}(\text{OH})]^+ + \text{Z}_2\text{-Cu}^{2+} \rightarrow \text{Z}[\text{Cu}^{2+}\text{-O}^{2-}\text{-Cu}^{2+}]\text{-Z} + \text{Z-H}^+$ ) accompanied by the formation of  $\text{NH}_4^+$  ions ( $\text{Z-H}^+ + \text{NH}_3 \rightarrow \text{Z-NH}_4^+$ ) was present in  $\text{Cu}_x/\text{CHA}$  during the heating process. The intra-zeolite oxolation process in Cu-SSZ-13 has been proven by Mozgawa et al. [40]. Of note, the  $\text{NH}_4^+$  generation was positively correlated with the Cu content. We further investigated the correlation between the degree of the intra-zeolite oxolation process and the content of Cu species, as depicted in Fig. S8. The results showed that the degree of the intra-zeolite oxolation process was more strongly correlated with the content of  $\text{Z}[\text{Cu}(\text{OH})]^+$  species compared to the content of  $\text{CuO}_x$  and  $\text{Z}_2\text{-Cu}^{2+}$ . This indicated that the higher  $\text{Z}[\text{Cu}(\text{OH})]^+$  species content in  $\text{Cu}_x/\text{CHA}$ , the easier the intra-zeolite oxolation process in  $\text{Cu}_x/\text{CHA}$  could be carried out. Hence, it is reasonable to believe that the intra-zeolite oxolation process was the main reason for the increase of the C peak in  $\text{NH}_3$ -TPD.

#### 3.3.2. $\text{NO}_x$ -TPD

Fig. S9 presents the  $\text{NO}_x$ -TPD profiles of  $\text{Cu}_x/\text{CHA}$ . All samples showed a weak  $\text{NO}_x$  desorption peak below 200 °C and an obvious  $\text{NO}_x$  desorption peak (mainly composed of  $\text{NO}_2$ ) above 300 °C, which were caused by the decomposition of adsorbed nitrite and nitrate species (including thermally stable bridged and bidentate nitrate species), respectively [41,42]. In addition, the  $\text{NO}_x$  desorption peak of  $\text{Cu}_x/\text{CHA}$  shifted toward higher temperature with increasing Cu content, suggesting that the introduction of Cu promoted higher stability nitrate formation. As shown in Fig. S9(b), the total  $\text{NO}_x$  desorption of  $\text{Cu}_x/\text{CHA}$  increased from 26.8 to 126.4  $\mu\text{mol/g}$  as the Cu content increased from 0.97 to 4.7 wt%. These results demonstrated that the existence of Cu promoted nitrate species production, which were dependent on the Cu content.

### 3.4. $\text{NH}_3$ -SCR performance

The NO conversion of  $\text{Cu}_x/\text{CHA}$  at reaction temperature between 90 and 650 °C are shown in Fig. 5(a) and S10. Pure H-SSZ-13 catalyst showed poor SCR activity that the NO conversion could not reach 60 % even at 650 °C (Fig. S10(a)). The presence of Cu significantly improved the  $\text{NH}_3$ -SCR and  $\text{N}_2$  selectivity (~99 %) over H-SSZ-13. With increasing Cu content from 0.97 wt% to 2.9 wt%, the NO conversion which was above 90 % ( $T_{90}$ ) of  $\text{Cu}_x/\text{CHA}$  in the low-temperature range decreased from 260 °C to 180 °C. Further increasing Cu content to 4.7 wt%, the  $T_{90}$  increased slightly. However, for the high-temperature activity (>400 °C) of  $\text{Cu}_x/\text{CHA}$ , the  $\text{NH}_3$ -SCR activities decreased with the increase of Cu content due to non-selective  $\text{NH}_3$  oxidation, which had been demonstrated in previous studies [43]. In addition,  $\text{N}_2\text{O}$  concentration increased with increasing Cu content (Fig. S10(b)).

Furthermore, we also studied the kinetic activation energy ( $E_a$ ) of the  $\text{Cu}_x/\text{CHA}$ , as shown in Fig. 5(b). The apparent activation energies increased slightly from 26 to 42 kJ/mol with the increase of Cu content (from 0.97 to 4.7 wt%), and a similar trend was found in previous studies [18], which was probably due to the fact that the higher the copper content, the more significant internal diffusion limitation within the zeolite. Moreover, the influence of copper content on the rate in the low-temperature range were investigated and shown in Fig. 5(c). The reaction rate of  $\text{Cu}_x/\text{CHA}$  increased linearly with increasing the Cu

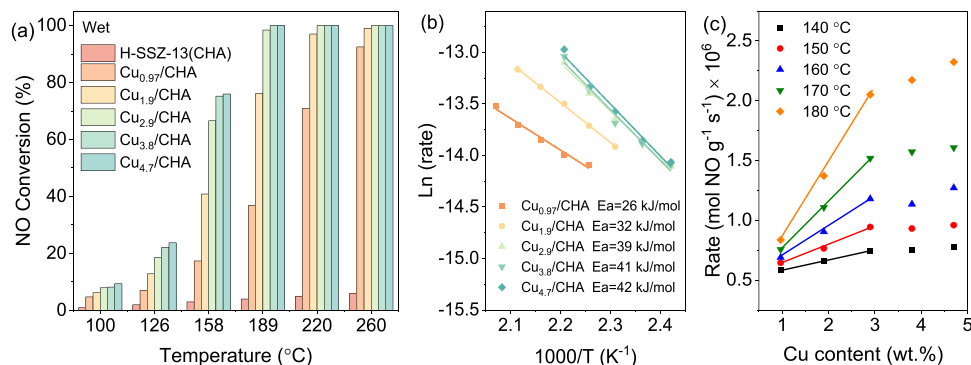


Fig. 5. (a) NO conversion of Cu<sub>x</sub>/CHA catalysts; (b) Arrhenius plots for standard SCR in the low-temperature range (< 200 °C) on Cu<sub>x</sub>/CHA catalysts; (c) SCR rates as a function of Cu content in different reaction temperatures.

content from 0.97 to 2.9 wt%, whereas it varied nonlinearly when the Cu content was higher than 2.9 wt%. According to the Koros-Nowak criterion, the linear relationship indicated that the reaction was run in the kinetic regime which excludes transfer limitations [44]. Gao et al. [44] also found that the Koros-Nowak criterion hold at moderate Cu contents (0.378 wt% - 3.43 wt%) and that mass-transfer limitations were the primary reason why high Cu content catalysts did not follow the Koros-Nowak criterion. Due to mass-transfer limitations, it is difficult to determine whether a uniform reaction path was followed on Cu<sub>x</sub>/CHA from the apparent activation energies alone. Therefore, we

further investigated the effect of Cu content on the reaction mechanism of Cu<sub>x</sub>/CHA by using in situ DRIFTS.

### 3.5. In situ DRIFTS study of the reaction mechanism

#### 3.5.1. Adsorption of NO<sub>x</sub> followed by exposure to NH<sub>3</sub>

Fig. 6(a) and S11 demonstrated the NO/O<sub>2</sub> adsorption on the four Cu<sub>x</sub>/CHA catalysts at 150 °C. The main adsorbed species of NO<sub>x</sub> include bridging nitrate (~1625 cm<sup>-1</sup>) [45], monodentate nitrate linked to Al sites (~1595 cm<sup>-1</sup>) [27], monodentate nitrate linked to Cu sites (~

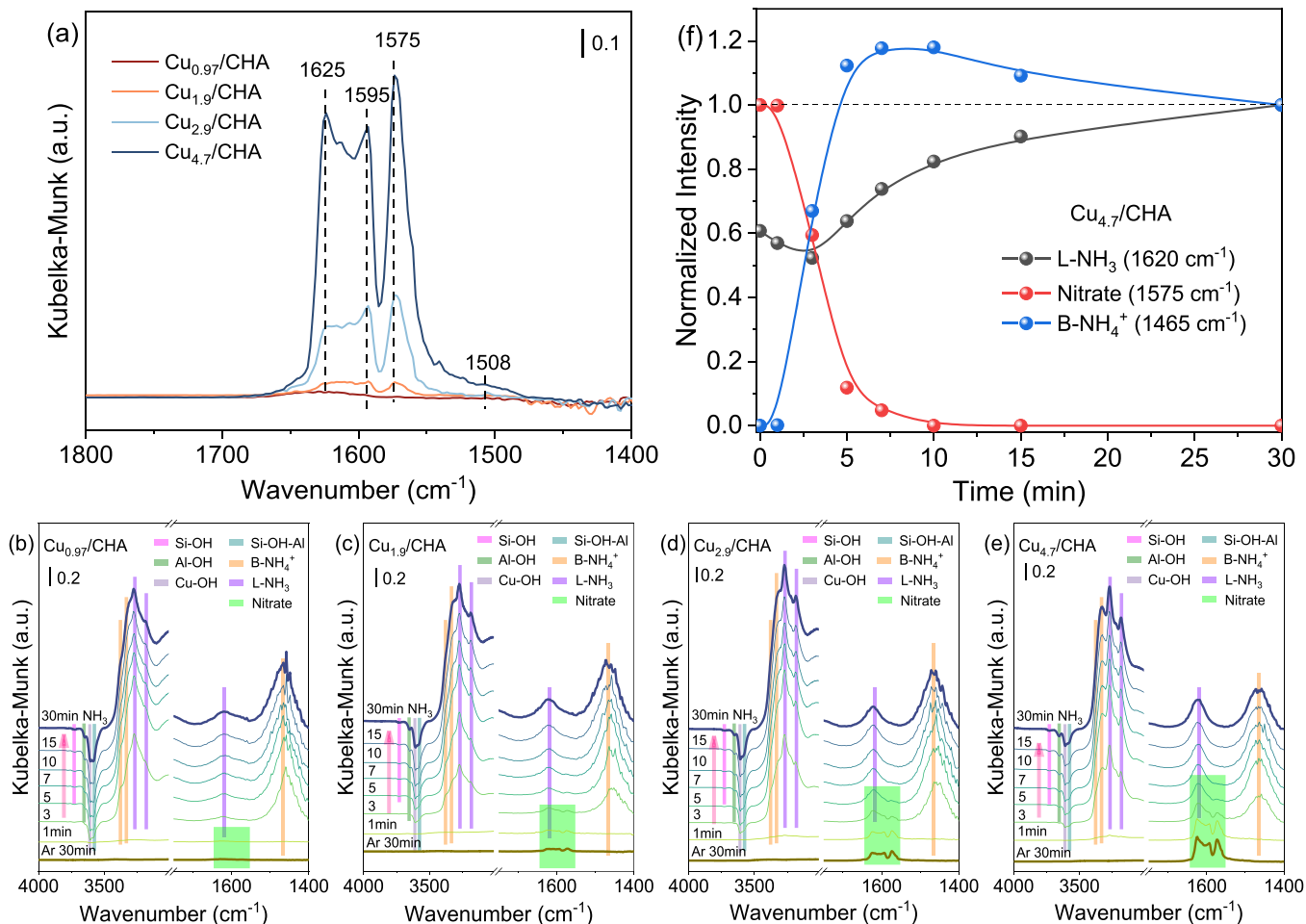


Fig. 6. (a) In situ DRIFTS spectra of Cu<sub>x</sub>/CHA at 150 °C in 1000 ppm NO + 5 vol% O<sub>2</sub> atmosphere after 60 min; (b-e) In situ DRIFTS of 1000 ppm NH<sub>3</sub> and pre-adsorbed NO + 5 vol% O<sub>2</sub> species at 150 °C on (b) Cu<sub>0.97</sub>/CHA, (c) Cu<sub>1.9</sub>/CHA, (d) Cu<sub>2.9</sub>/CHA, and (e) Cu<sub>4.7</sub>/CHA; (f) Normalized band areas associated with the DRIFTS results in Fig. 6(e).

1575  $\text{cm}^{-1}$ ) [28], and  $\text{NO}_2$  ( $\sim 1508 \text{ cm}^{-1}$ ) [45].

As shown in Fig. S11, the nitrate intensity of  $\text{Cu}_x/\text{CHA}$  increased with increasing  $\text{NO}+\text{O}_2$  flux time. In addition, bridging nitrate was formed more readily on catalysts with lower copper content than monodentate nitrate. The nitrate (especially the monodentate nitrates linked to Cu sites) increased remarkably with increasing the content of Cu, suggesting that increasing Cu content was beneficial to produce nitrate species on the catalyst, which was consistent with the results of  $\text{NO}+\text{O}_2$ -TPD (Fig. S9). Otherwise, those results demonstrated that although the increase in Cu content enhanced the generation of nitrate, the type of nitrate species on the samples did not change dramatically during the  $\text{NO}+\text{O}_2$  adsorption.

The reactions among the  $\text{NH}_3$  and adsorbed  $\text{NO}_x$  species was obtained and shown in Fig. 6(b)–(e). A similar trend was found in all four  $\text{Cu}_x/\text{CHA}$ , i.e., the band strength of the nitrate ( $1500\text{--}1700 \text{ cm}^{-1}$ ) decreased rapidly with increasing time of  $\text{NH}_3$  introduction, accompanying the forming of adsorbed  $\text{NH}_3$  species. To better understand the changes on  $\text{NO}_x$  species with increasing  $\text{NH}_3$  introduction time, the band areas of adsorbed nitrate and  $\text{NH}_3$  species on  $\text{Cu}_{4.7}/\text{CHA}$  were further normalized, and summarized in Fig. 6(f).

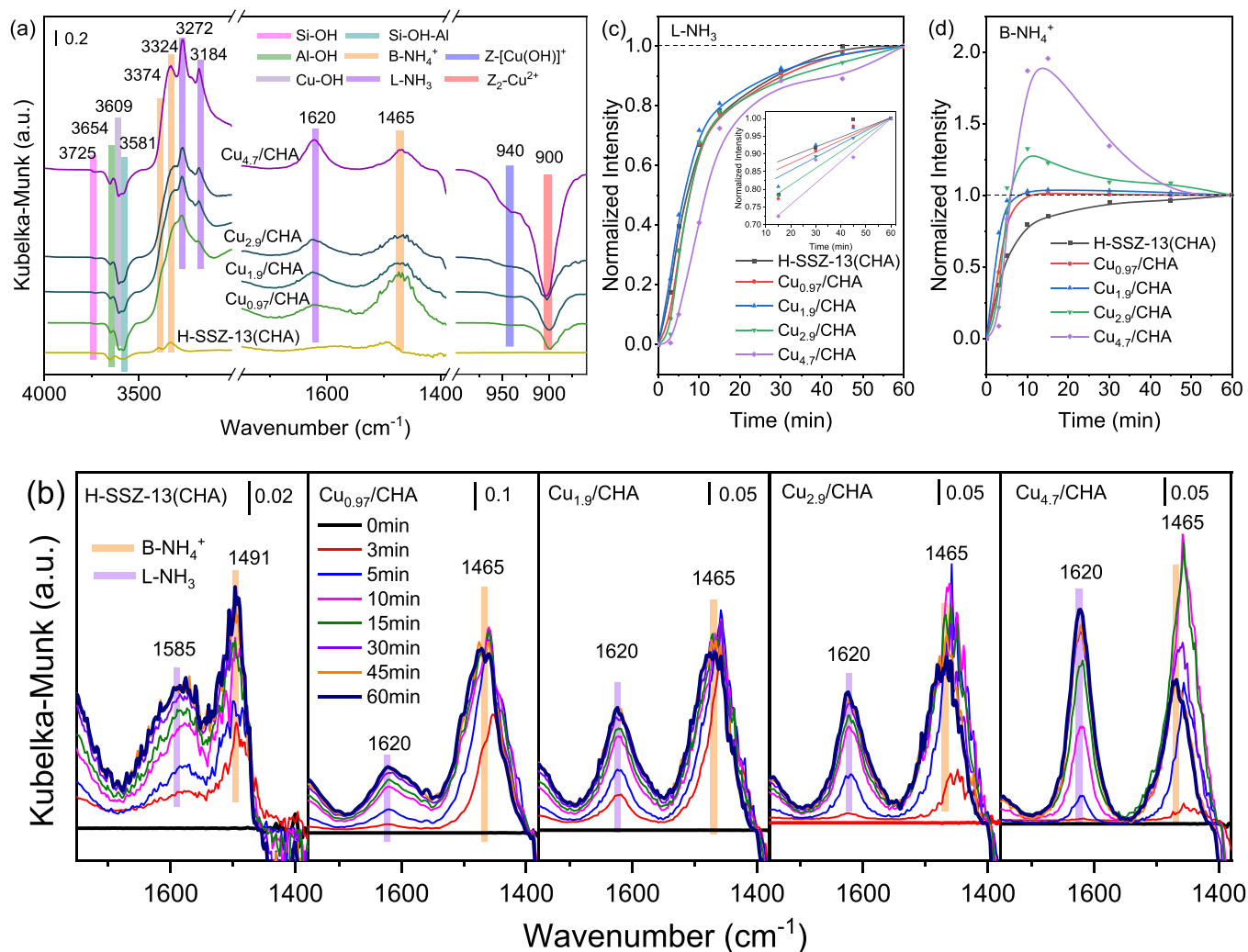
Of note, the band area at  $1620 \text{ cm}^{-1}$  decreased slightly after 1 min of 1000 ppm  $\text{NH}_3/\text{Ar}$  introduction, while the band area at  $1575 \text{ cm}^{-1}$  did not change significantly. The absence of the adsorbed  $\text{NH}_3$  species bands at this time, suggesting that the decrease at  $1620 \text{ cm}^{-1}$  might be due to the reaction between adsorbed  $\text{NO}_x$  species and gas-phase  $\text{NH}_3$ , which is

in accordance with the E-R mechanism. After 3 min of introduction of 1000 ppm  $\text{NH}_3/\text{Ar}$ , distinct bands associated with adsorbed  $\text{NH}_3$  species were formed. With the formation of adsorbed  $\text{NH}_3$  species, the adsorbed nitrate species decreased rapidly until they disappeared completely, which was due to the fact that the adsorbed nitrate species could react with the surface-adsorbed  $\text{NH}_3$ , which is in accordance with the L-H mechanism [35]. In addition, the band area of  $1620 \text{ cm}^{-1}$  decreased and then increased with increasing time of  $\text{NH}_3$  introduction, which might be caused by the fact that the spectral bands of both L- $\text{NH}_3$  and nitrate appeared near  $1620 \text{ cm}^{-1}$ .

Interestingly, the band area at  $1465 \text{ cm}^{-1}$  first increased and then decreased with increasing  $\text{NH}_3$  exposure time. However, to our knowledge, the content of adsorbed  $\text{NH}_3$  species increases with adsorption time until adsorption saturation. Therefore, we further investigated the adsorption characteristics of  $\text{Cu}_x/\text{CHA}$  on  $\text{NH}_3$  to reveal the intrinsic reason for the decrease in  $\text{NH}_3$  adsorption with increasing adsorption time.

### 3.5.2. Adsorption of $\text{NH}_3$ followed by exposure to $\text{NO}_x$

The adsorption behavior of  $\text{NH}_3$  on  $\text{Cu}_x/\text{CHA}$  at  $150^\circ\text{C}$  was investigated using the *in situ* DRIFTS technique and the results are shown in Fig. 7 and S12. The negative band at  $3725$ ,  $3654$ ,  $3609$ , and  $3581 \text{ cm}^{-1}$  were related to the O-H stretching vibrations of Si-OH, Al-OH, Cu-OH, and Si-OH-Al in the sample, respectively [27,38]. The bands at  $3100\text{--}3400 \text{ cm}^{-1}$  and  $1400\text{--}1700 \text{ cm}^{-1}$  were related to the stretching



**Fig. 7.** (a) *In situ* DRIFTS spectra of  $\text{Cu}_x/\text{CHA}$  at  $150^\circ\text{C}$  in 1000 ppm  $\text{NH}_3/\text{Ar}$  atmosphere after 60 min. (b) *In situ* DRIFTS spectra of  $\text{Cu}_x/\text{CHA}$  at  $150^\circ\text{C}$  in 1000 ppm  $\text{NH}_3/\text{Ar}$  atmosphere. (c) and (d) Normalized band areas associated with (b).

vibrations and bending vibrations of N-H in adsorbed  $\text{NH}_3$  species, respectively [27]. As shown in Fig. 7(a) and S12(a), the bands at 3396, 3334, and  $1491\text{ cm}^{-1}$  in H-SSZ-13(CHA) were assigned to the bending vibrations of N-H in adsorbed  $\text{NH}_4^+$  ( $\text{B-NH}_4^+$ ), while the bands at  $1585\text{ cm}^{-1}$  in H-SSZ-13(CHA) was assigned to the bending vibrations of N-H in  $\text{NH}_3$  ( $\text{L-NH}_3$ ) [28]. For Cu-containing zeolite ( $\text{Cu}_x/\text{CHA}$ ), several new bands were found at 3609, 3272, 3184, 1620, and  $1465\text{ cm}^{-1}$ , where those bands at 3272, 3184, and  $1620\text{ cm}^{-1}$  were related to the coordinated  $\text{NH}_3$  molecule on the isolated  $\text{Cu}^{2+}$  ions ( $\text{L-NH}_3$ ) [46], while the band at  $1465\text{ cm}^{-1}$  was assigned to the adsorbed  $\text{NH}_4^+$  on the Brønsted acid sites ( $\text{B-NH}_4^+$ ) [28]. The bands at 940 and  $900\text{ cm}^{-1}$  were ascribed to T-O-T vibrations on the  $\text{Z}[\text{Cu}(\text{OH})]^+$  and  $\text{Z}_2\text{-Cu}^{2+}$  species, respectively [47].

The trends of  $\text{NH}_3$  adsorbed species on H-SSZ-13(CHA) and  $\text{Cu}_x/\text{CHA}$  with increasing  $\text{NH}_3$  adsorption time are shown in Fig. 7(b). The peak intensity at  $1585\text{ cm}^{-1}$  ( $\text{L-NH}_3$ ) and  $1491\text{ cm}^{-1}$  ( $\text{B-NH}_4^+$ ) on H-SSZ-13(CHA) increased significantly in the first 15 min, after that the increasing rate of  $\text{B-NH}_4^+$  and  $\text{L-NH}_3$  slowed down, but its intensity increased continuously to the near adsorption balance in 60 min. Those results indicated that monotonically increasing trends with the increase of  $\text{NH}_3$  adsorption time could reach saturation after 60 min.

Interestingly, for the Cu-containing zeolite ( $\text{Cu}_x/\text{CHA}$ ), the adsorbed  $\text{NH}_3$  species (especially  $\text{B-NH}_4^+$ ) showed a different trend from that of H-SSZ-13(CHA) as the adsorption time increased. To make this difference in variation clearer, the peak area at  $\sim 1620\text{ cm}^{-1}$  ( $\text{L-NH}_3$ ) and  $\sim 1465\text{ cm}^{-1}$  ( $\text{B-NH}_4^+$ ) after 60 min of adsorption was normalized and the variation of adsorption peak areas with adsorption time are shown in Fig. 7(c) and (d), respectively. The peak area of  $\text{L-NH}_3$  on  $\text{Cu}_x/\text{CHA}$  (Fig. 7(c)) increased significantly in the first 15 min, which should be aroused by the rapid adsorption of  $\text{NH}_3$  on the isolated  $\text{Cu}^{2+}$  ions sites. After 15 min, the increasing rate of  $\text{L-NH}_3$  slowed down until the adsorption equilibrium was approached at 60 min. In general,  $\text{B-NH}_4^+$  should show a similar change to  $\text{L-NH}_3$  until adsorption saturation with increasing adsorption time [35]. However, the peak areas of  $\text{B-NH}_4^+$  on  $\text{Cu}_x/\text{CHA}$  (Fig. 7(d)) showed different trends, i.e., the peak areas of  $\text{B-NH}_4^+$  increased with increasing  $\text{NH}_3$  exposing time in the form of a volcano curve, which reached the maximum after adsorption for about 15 min. Notably, after 15 min, the peak areas of  $\text{B-NH}_4^+$  did not show the expected increase but rather a decrease, which seems to indicate that part of the  $\text{B-NH}_4^+$  was converted to  $\text{L-NH}_3$  with increasing adsorption time. In addition, the decreasing trend was more pronounced with the increase in Cu content, which suggested that this trend seemed to be associated with the Cu species in the catalysts and positively correlated with the Cu content.

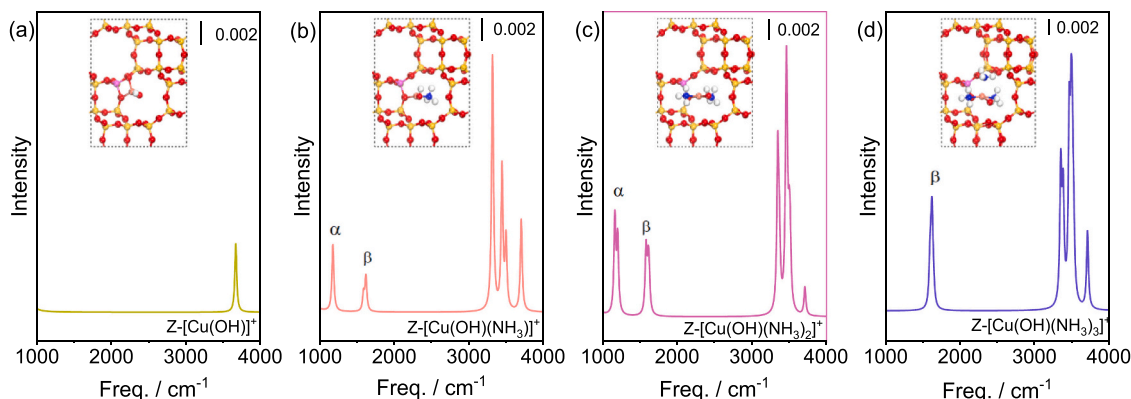
Among three different Cu species in  $\text{Cu}_x/\text{CHA}$ , the  $\text{NH}_3$  was barely adsorbed on  $\text{CuO}_x$  species (Fig. S13), suggesting that this trend depended on  $\text{Z}_2\text{-Cu}^{2+}$  and/or  $\text{Z}[\text{Cu}(\text{OH})]^+$ . Combined with the  $\text{H}_2$ -TPR results, we further investigated the correlation between the degree of

increase in  $\text{B-NH}_4^+$  and the content of Cu species, and the results are plotted in Fig. S14. These results indicated that the content of  $\text{Z}[\text{Cu}(\text{OH})]^+$  species was more readily linearly correlated with the degree of increase in  $\text{B-NH}_4^+$  than the content of  $\text{Z}_2\text{-Cu}^{2+}$  species. Hence, It was reasonable to hypothesize that  $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)_x]^+$  ( $x < 3$ ) might exhibit analogous properties to  $\text{B-NH}_4^+$ , but it will convert to  $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)_3]^+$  with increasing  $\text{NH}_3$  adsorption time and exhibiting more  $\text{L-NH}_3$  properties. Based on this conjecture, we also performed DFT theoretical calculations of the  $\text{NH}_3$  adsorption process on  $\text{Z}[\text{Cu}(\text{OH})]^+$  and simulated the IR spectra on  $\text{Z}[\text{Cu}(\text{OH})]^+$  with different  $\text{NH}_3$  adsorption amounts, the results are shown in Fig. 8 and S15. Two N-H vibrational peaks ( $\alpha$  and  $\beta$ ) were generated with  $\text{NH}_3$  adsorption, and the  $\alpha$  peak disappeared when  $\text{NH}_3$  adsorption was saturated. These results proved the previous conjecture that  $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)_x]^+$  ( $x < 3$ ) exhibited not only  $\text{L-NH}_3$  properties, but also properties similar to those of  $\text{B-NH}_4^+$ . However, when  $\text{NH}_3$  adsorption was saturated ( $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)_3]^+$ ), it would exhibit more  $\text{L-NH}_3$  properties.

Following  $\text{NH}_3$  adsorption, the catalyst was purged with argon at  $150^\circ\text{C}$  for 30 min to eliminate physically adsorbed  $\text{NH}_3$ , and then a 1000 ppm NO and 5 vol%  $\text{O}_2/\text{Ar}$  gas mixture was introduced. Finally, recorded the spectra and summarized in Fig. 9 and S16–17. With introducing  $\text{NO} + \text{O}_2$ , the  $\text{NH}_3$  adsorbed species ( $3100\text{--}3400\text{ cm}^{-1}$ ) gradually decreased, and when the exposure time exceeded 45 min, new bands were formed progressively at  $1500\text{--}1700\text{ cm}^{-1}$ , which are widely regarded as the surface nitrate or nitro species adsorbed primarily on the Cu species of catalyst [45].

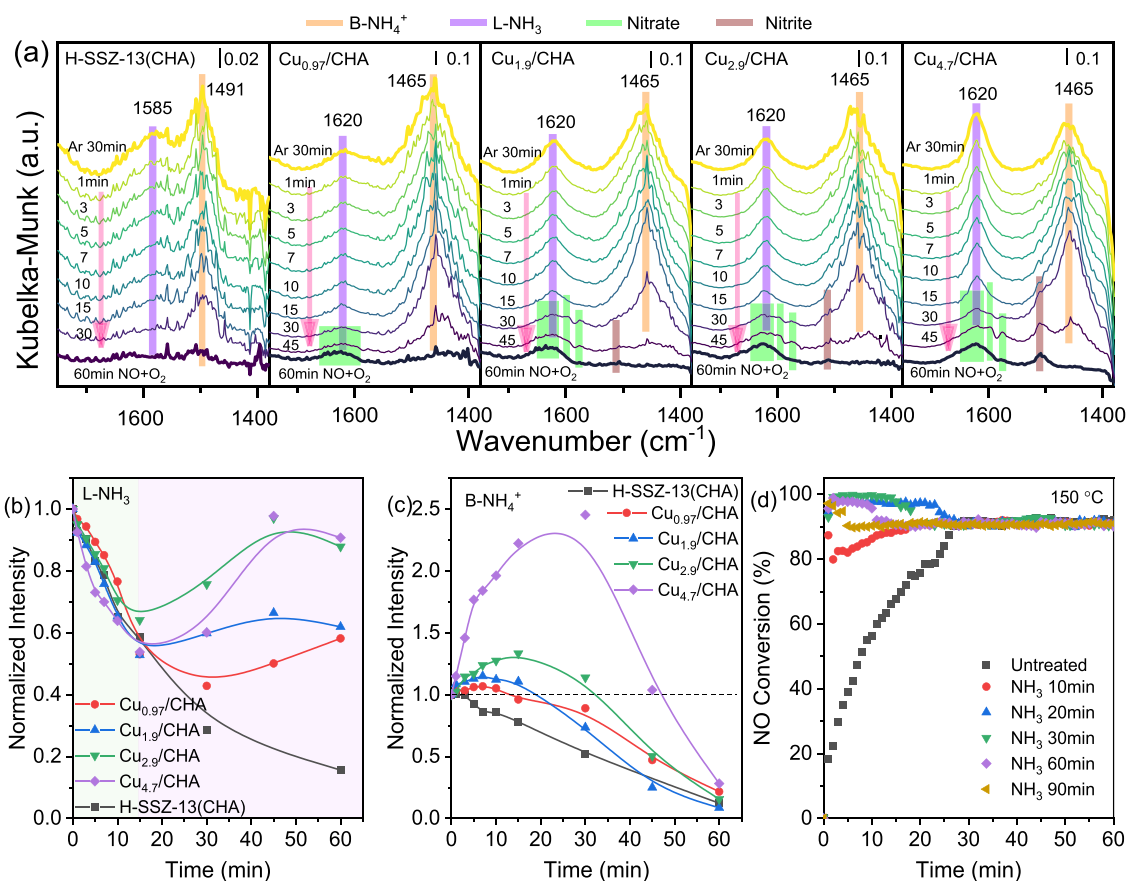
For a better understanding of the trend of  $\text{NH}_3$  adsorbed species with  $\text{NO} + \text{O}_2$  exposure time, the band areas at  $\sim 1620\text{ cm}^{-1}$  ( $\text{L-NH}_3$ ) and  $\sim 1465\text{ cm}^{-1}$  ( $\text{B-NH}_4^+$ ) were normalized to assess the reactivity of  $\text{NO} + \text{O}_2$  with  $\text{NH}_3$  adsorbed at different sites, and plotted in Fig. 9(b) and (c), respectively. For H-SSZ-13, the bands at  $1585\text{ cm}^{-1}$  ( $\text{L-NH}_3$ ) and  $1491\text{ cm}^{-1}$  ( $\text{B-NH}_4^+$ ) decreased with the introduction of NO and  $\text{O}_2$ . Moreover, for Cu-containing zeolite samples, the band areas at  $1620\text{ cm}^{-1}$  ( $\text{L-NH}_3$ ) reduced substantially within the first 15 min with introducing  $\text{NO} + \text{O}_2$ , indicating that adsorbed  $\text{NH}_3$  species on the Lewis acid sites (including  $\text{NH}_3$  adsorbed at  $\text{Z}_2\text{-Cu}^{2+}$  and  $\text{Z}[\text{Cu}(\text{OH})]^+$ ) could be reacted with the  $\text{NO}/\text{O}_2$  mixture, and the  $\text{NH}_3$  adsorbed on the  $\text{Z}[\text{Cu}(\text{OH})]^+$  has higher reaction performance than that of  $\text{Z}_2\text{-Cu}^{2+}$  (as shown in Fig. S17, the decreasing rate of  $\text{NH}_3$  on  $\text{Z}[\text{Cu}(\text{OH})]^+$  was greater than that on  $\text{Z}_2\text{-Cu}^{2+}$ ). Following 15 min, the band area of  $1620\text{ cm}^{-1}$  increased as the time of introduction of  $\text{NO} + \text{O}_2$  increased, probably due to the generation of nitrate on the surface.

More interestingly,  $\text{B-NH}_4^+$  on  $\text{Cu}_x/\text{CHA}$  increased with increasing  $\text{NO} + \text{O}_2$  adsorption time, and the increase was more pronounced with higher copper content (Fig. 9(c)). However, there was a simultaneous increase in the intensity of Si-OH-Al (Fig. S16), suggesting that the  $\text{NH}_3$  adsorbed on the Brønsted acid sites was released, which should lead to a decrease in  $\text{B-NH}_4^+$ . It contradicted the increased intensity of  $\text{B-NH}_4^+$  in

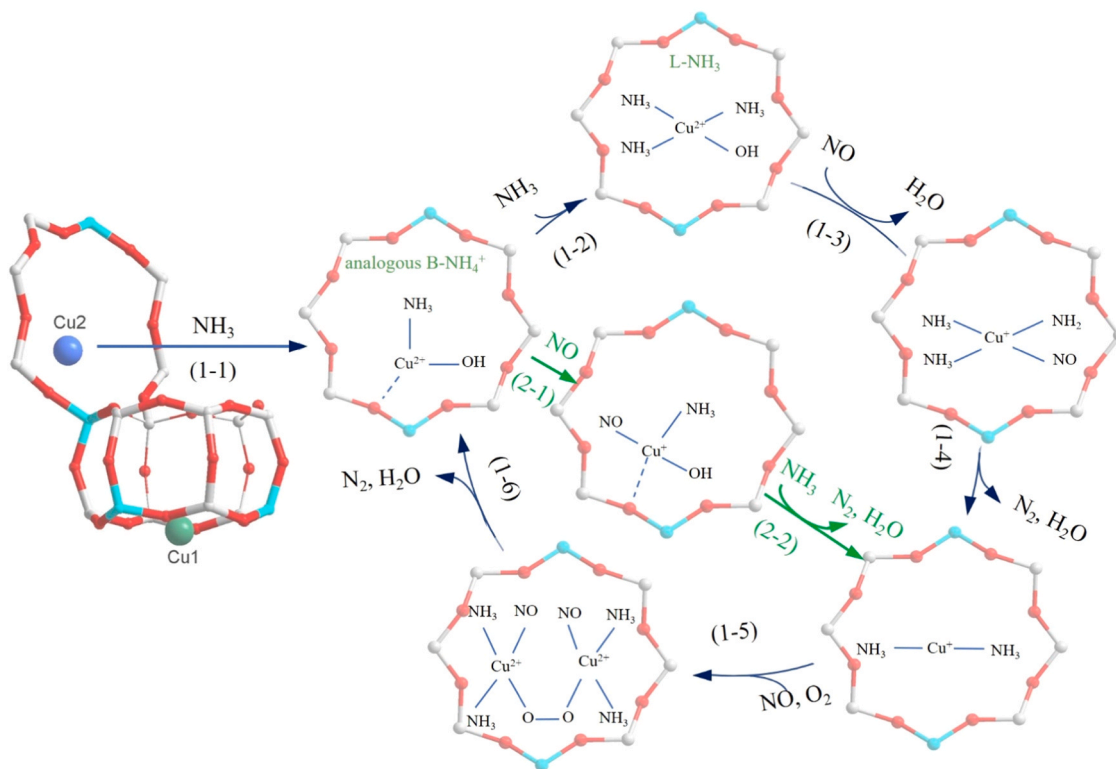


**Fig. 8.** Infrared vibrational spectra of structural simulations obtained by DFT calculations. (a)  $\text{Z}[\text{Cu}(\text{OH})]^+$ , (b)  $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)]^+$ , (c)  $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)_2]^+$ , (d)  $\text{Z}[\text{Cu}(\text{OH})(\text{NH}_3)_3]^+$ .





**Fig. 9.** (a) In situ DRIFTS of 1000 ppm NO + 5 vol% O<sub>2</sub> and pre-adsorbed NH<sub>3</sub> species at 150 °C on Cu<sub>x</sub>/CHA samples; (b) and (c) Normalized band areas associated with (a); (d) NH<sub>3</sub>-SCR performance of Cu<sub>4.7</sub>/CHA samples pretreated with different NH<sub>3</sub> adsorption time; Reactant feed contains 500 ppm NO, 500 ppm NH<sub>3</sub>, and 5 vol% O<sub>2</sub> balanced with Ar at a weight hourly space velocity (WHSV) of 180,000 mL.h<sup>-1</sup>.g<sup>-1</sup>.



**Fig. 10.** The possible reaction pathway of the NH<sub>3</sub>-SCR cycle at Z-[Cu(OH)]<sup>+</sup> sites.

Fig. 9(c), demonstrating there were other pathways for the formation of  $\text{B-NH}_4^+$  during the reaction, which were closely related to the Cu content.

From the overall reaction, the  $\text{NH}_3$  adsorbed at L- and B-acid sites should eventually decrease with the increase of reaction time and reaction temperature. In addition, the  $\text{B-NH}_4^+$  had been demonstrated not to be directly involved in the reaction with  $\text{NO}_x$ , but to supply candidate  $\text{NH}_3$  for the Cu site [14]. The increased content of  $\text{NH}_4^+$  on the surface during the reaction demonstrated the producing rate of  $\text{B-NH}_4^+$  was faster than that of consumption. Paolucci et al. [11] demonstrated by the first-principles thermodynamics and spectroscopies that L- $\text{NH}_3$  species ( $\text{Z}_2\text{-Cu}^{2+}$  species) reaction with NO generated new  $\text{NH}_4^+$  species (see steps (1–3) in Fig. S18). On the other hand, as shown in the  $\text{NH}_3$  adsorption process (Fig. 7), we found that the unsaturated adsorbed  $\text{Z-[Cu(OH)]}^+$  species ( $\text{Z-[Cu(OH)(NH}_3)_x]^+$  ( $x < 3$ )) exhibited properties similar to those of  $\text{B-NH}_4^+$ , which led to an increase in  $\text{B-NH}_4^+$ . To verify which Cu species were responsible for this phenomenon, we investigated the correlation between the degree of  $\text{B-NH}_4^+$  increase during the reaction and the content of Cu species (Fig. S19). The results showed that the correlation between the degree of  $\text{B-NH}_4^+$  increase during the reaction and the  $\text{Z-[Cu(OH)]}^+$  species was higher than that of  $\text{Z}_2\text{-Cu}^{2+}$  species. Therefore, part of the increase in  $\text{B-NH}_4^+$  came from  $\text{Z-[Cu(OH)]}^+$ , which were caused by the reaction of saturated adsorbed  $\text{Z-[Cu(OH)(NH}_3)_3]^+$  species with  $\text{NO} + \text{O}_2$  to produce unsaturated adsorbed  $\text{Z-[Cu(OH)(NH}_3)_x]^+$  ( $x < 3$ ) species (following steps (1–3)-(1–6) in Fig. 10).

For  $\text{Cu}_x/\text{CHA}$ , there were three main Cu species,  $\text{Z}_2\text{-Cu}^{2+}$ ,  $\text{Z-[Cu(OH)]}^+$ , and  $\text{CuO}_x$ . It was generally believed that  $\text{Z-[Cu(OH)]}^+$  had higher low-temperature reactivity and that pairs of  $\text{NH}_3$ -solvated Cu species dynamically combine to form  $\text{NH}_3$ -SCR active sites at low temperatures [11,18,20]. However, in fact, as mentioned above, different  $\text{NH}_3$  coordination numbers on  $\text{Z-[Cu(OH)]}^+$  could exhibit different properties, which directly affect the reaction performance of the catalyst. Hence, it was reasonable to believe that not only the content of  $\text{Z-[Cu(OH)]}^+$  species, but also the degree of  $\text{NH}_3$  coordination of  $\text{Z-[Cu(OH)]}^+$  species affect the performance of the low-temperature  $\text{NH}_3$ -SCR reaction. To prove this conjecture, we investigated the effect of different  $\text{NH}_3$  pre-adsorption times on the  $\text{NH}_3$ -SCR performance of  $\text{Cu}_{4.7}/\text{CHA}$  samples, and the results are shown in Fig. 9(d) and S20. After  $\text{NH}_3$  pre-adsorption, the NO conversion of the  $\text{Cu}_{4.7}/\text{CHA}$  samples was significantly increased, especially in the first 30 min, indicating that the catalysts after  $\text{NH}_3$  pre-adsorption had higher  $\text{NH}_3$ -SCR reaction performance than the untreated catalysts. However, with the increase of  $\text{NH}_3$  pre-adsorption time, the NO conversion first increased and then decreased, indicating a decrease in activity after saturation of  $\text{NH}_3$  adsorption. Those results suggested that the unsaturated adsorbed species ( $\text{Z-[Cu(OH)(NH}_3)_x]^+$  ( $x < 3$ )) probably exhibited higher reaction performance than saturated adsorbed  $\text{Z-[Cu(OH)(NH}_3)_3]^+$  species (following steps (2–1)-(2–2) in Fig. 10). This provided a new idea to improve the catalyst conversion in practical applications (cold start) by pre-adsorbing  $\text{NH}_3$  to ensure that NO reacted quickly.

Furthermore, the application of the reaction mechanism depended mainly on the catalyst systems and the reaction conditions, for example, the reaction gas composition and reaction temperature [48,49]. In this work, for the  $\text{Cu}_x/\text{CHA}$  catalyst, as shown in Figs. 6 and 9, the  $\text{NH}_3$ -SCR reaction process in the low-temperature region followed both the L-H mechanism (the adsorbed  $\text{NH}_3$  species react with the adsorbed  $\text{NO}_x$  species) and the E-R mechanism (the adsorbed  $\text{NH}_3$  species react with the gaseous  $\text{NO}_x$ ), as illustrated in Fig. 10.

#### 4. Conclusions

In this work, the Al-rich  $\text{Cu}_x/\text{CHA}$  catalysts were prepared by the IWI method, and the  $\text{NH}_3$ -SCR performance,  $\text{NH}_3$  dissolution process and  $\text{NH}_3$ -SCR catalytic mechanism of Cu active sites were investigated. The Al-rich  $\text{Cu}_x/\text{CHA}$  catalysts showed high NO conversion and  $\text{N}_2$  selectivity, and the NO conversion increased with increasing the Cu content. Characterization results showed that the  $\text{Z-[Cu(OH)]}^+$  content in the

$\text{Cu}_x/\text{CHA}$  samples gradually increased with the increase of copper content, which improved the low-temperature activity of the  $\text{Cu}_x/\text{CHA}$  samples. The  $\text{Z}_2\text{-Cu}^{2+}$  content increased first and then changed insignificantly. At Cu contents higher than 1.9 wt%,  $\text{CuO}_x$  species were produced, which lead to a decrease in the high-temperature activity of  $\text{Cu}_x/\text{CHA}$ . And the higher the Cu content, the higher the content of  $\text{CuO}_x$  species. These results suggested that high Cu content promoted the formation of  $\text{Z-[Cu(OH)]}^+$  and  $\text{CuO}_x$  particles. In addition, the high Cu content not only improved the adsorption capacity of  $\text{NO}_x$  but also increased the intra-zeolite oxolation process in the  $\text{Cu}_x/\text{CHA}$  catalysts, which led to an increase in the acid content associated with the Brønsted acid sites in the  $\text{NH}_3$ -TPD with the increase of Cu content. *In situ* DRIFTS were utilized to detect the adsorption and reaction properties of the  $\text{Cu}_x/\text{CHA}$  catalysts on the reactants and to investigate the reaction mechanism. The results suggested that the  $\text{Z-[Cu(OH)(NH}_3)_x]^+$  ( $x < 3$ ) might exhibit analogous properties to  $\text{B-NH}_4^+$ , but it will convert to  $\text{Z-[Cu(OH)(NH}_3)_3]^+$  with increasing  $\text{NH}_3$  adsorption time and exhibit more L- $\text{NH}_3$  properties. Moreover, not only the content, but also the degree of  $\text{NH}_3$  coordination of  $\text{Z-[Cu(OH)]}^+$  species affects the performance of the low-temperature  $\text{NH}_3$ -SCR reaction. Those findings might provide a new insight into understanding the role of  $\text{B-NH}_4^+$  in low-temperature reactions.

#### CRedit authorship contribution statement

**Yali Shen:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Zhiqiang Wang:** Software, Investigation, Formal analysis. **Shasha Ge:** Methodology, Investigation. **Li Wang:** Validation, Methodology. **Wangcheng Zhan:** Visualization, Funding acquisition. **Qiguang Dai:** Visualization, Validation. **Yanglong Guo:** Resources, Project administration. **Yun Guo:** Writing – review & editing, Supervision. **Aiyong Wang:** Writing – review & editing, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgements

This work was supported by the National Key Research and Development Program of China (2023YFA1508500), the National Natural Science Foundation of China (22106101, U21A20326), and the Fundamental Research Funds for the Central Universities.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124094.

#### References

- [1] Y. Wu, W. Zhao, S.H. Ahn, Y. Wang, E.D. Walter, Y. Chen, M.A. Derewinski, N. M. Washton, K.G. Rappe, Y. Wang, D. Mei, S.B. Hong, F. Gao, Interplay between copper redox and transfer and support acidity and topology in low temperature  $\text{NH}_3$ -SCR, Nat. Commun. 14 (2023) 2633, <https://doi.org/10.1038/s41467-023-38309-8>.
- [2] Y. Shan, G. He, J. Du, Y. Sun, Z. Liu, Y. Fu, F. Liu, X. Shi, Y. Yu, H. He, Strikingly distinctive  $\text{NH}_3$ -SCR behavior over  $\text{Cu-SSZ-13}$  in the presence of  $\text{NO}_2$ , Nat. Commun. 13 (2022) 4606, <https://doi.org/10.1038/s41467-022-32136-z>.
- [3] T. Andana, K.G. Rappe, N.C. Nelson, F. Gao, Y. Wang, Selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$  over Ce-Mn oxide and  $\text{Cu-SSZ-13}$  composite catalysts – low

- temperature enhancement, *Appl. Catal. B: Environ.* (2022) 121522, <https://doi.org/10.1016/j.apcatb.2022.121522>.
- [4] X. Ye, J.E. Schmidt, R.P. Wang, I.K. van Ravenhorst, R. Oord, T. Chen, F. de Groot, X. Ye, B.M. Weckhuysen, Deactivation of Cu-exchanged automotive-emission NH<sub>3</sub>-SCR catalysts elucidated with nanoscale resolution using scanning transmission X-ray microscopy, *Angew. Chem. Int. Ed.* 59 (2020) 15610–15617, <https://doi.org/10.1002/anie.201916554>.
  - [5] B. Peng, K.G. Rappé, Y. Cui, F. Gao, J. Szanyi, M.J. Olszta, E.D. Walter, Y. Wang, J. D. Holladay, R.A. Goffe, Enhancement of high-temperature selectivity on Cu-SSZ-13 towards NH<sub>3</sub>-SCR reaction from highly dispersed ZrO<sub>2</sub>, *Appl. Catal. B: Environ.* 263 (2020) 118359, <https://doi.org/10.1016/j.apcatb.2019.118359>.
  - [6] D. Chen, Y. Yan, A. Guo, V. Rizzotto, H. Lei, Z. Qiao, H. Liang, M. Jabłońska, X. Jiang, J. Jiang, R. Palkovits, P. Chen, D. Ye, U. Simon, Mechanistic insights into the promotion of low-temperature NH<sub>3</sub>-SCR catalysis by copper auto-reduction in Cu-zeolites, *Appl. Catal. B: Environ.* 322 (2023) 122118, <https://doi.org/10.1016/j.apcatb.2022.122118>.
  - [7] V.V. Mesilov, S.L. Bergman, S. Dahlin, Y. Xiao, S. Xi, M. Zhirui, L. Xu, W. Chen, L. J. Pettersson, S.L. Bernasek, Differences in oxidation-reduction kinetics and mobility of Cu species in fresh and SO<sub>2</sub>-poisoned Cu-SSZ-13 catalysts, *Appl. Catal. B: Environ.* 284 (2021) 119756, <https://doi.org/10.1016/j.apcatb.2020.119756>.
  - [8] L. Chen, T.V.W. Janssens, P.N.R. Vennestrom, J. Jansson, M. Skoglundh, H. Grönbeck, A complete multisite reaction mechanism for low-temperature NH<sub>3</sub>-SCR over Cu-CHA, *ACS Catal.* 10 (2020) 5646–5656, <https://doi.org/10.1021/acscatal.0c00440>.
  - [9] R. Daya, D.J. Deka, A. Goswami, U. Menon, D. Trandal, W.P. Partridge, S.Y. Joshi, A redox model for NO oxidation, NH<sub>3</sub> oxidation and high temperature standard SCR over Cu-SSZ-13, *Appl. Catal. B: Environ.* 328 (2023) 122524, <https://doi.org/10.1016/j.apcatb.2023.122524>.
  - [10] Y. Cui, Y. Wang, E.D. Walter, J. Szanyi, Y. Wang, F. Gao, Influences of Na<sup>+</sup> cation on the structure and performance of Cu/SSZ-13 selective catalytic reduction catalysts, *Catal. Today* 339 (2020) 233–240, <https://doi.org/10.1016/j.cattod.2019.02.037>.
  - [11] C. Paolucci, A.A. Parekh, I. Khurana, J.R. Di Iorio, H. Li, J.D. Albarracin Caballero, A.J. Shih, T. Anggara, W.N. Delgass, J.T. Miller, F.H. Ribeiro, R. Gounder, W. F. Schneider, Catalysis in a cage: condition-dependent speciation and dynamics of exchanged Cu cations in SSZ-13 zeolites, *J. Am. Chem. Soc.* 138 (2016) 6028–6048, <https://doi.org/10.1021/jacs.6b02651>.
  - [12] K.A. Lomachenko, E. Borfecchia, C. Negri, G. Berlier, C. Lamberti, P. Beato, H. Falsig, S. Bordiga, The Cu-CHA deNO<sub>x</sub> catalyst in action: Temperature-dependent NH<sub>3</sub>-assisted selective catalytic reduction monitored by operando XAS and XES, *J. Am. Chem. Soc.* 138 (2016) 12025–12028, <https://doi.org/10.1021/jacs.6b06809>.
  - [13] L. Ren, L. Zhu, C. Yang, Y. Chen, Q. Sun, H. Zhang, C. Li, F. Nawaz, X. Meng, F. S. Xiao, Designed copper-amine complex as an efficient template for one-pot synthesis of Cu-SSZ-13 zeolite with excellent activity for selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>, *Chem. Commun.* 47 (2011) 9789–9791, <https://doi.org/10.1039/c1cc12469b>.
  - [14] F. Gao, N.M. Washton, Y. Wang, M. Kollár, J. Szanyi, C.H.F. Peden, Effects of Si/Al ratio on Cu/SSZ-13 NH<sub>3</sub>-SCR catalysts: implications for the active Cu species and the roles of Brønsted acidity, *J. Catal.* 331 (2015) 25–38, <https://doi.org/10.1016/j.jcat.2015.08.004>.
  - [15] S.L. Bergman, S. Dahlin, V.V. Mesilov, Y. Xiao, J. Englund, S. Xi, C. Tang, M. Skoglundh, L.J. Pettersson, S.L. Bernasek, In-situ studies of oxidation/reduction of copper in Cu-CHA SCR catalysts: comparison of fresh and SO<sub>2</sub>-poisoned catalysts, *Appl. Catal. B: Environ.* 269 (2020) 118722, <https://doi.org/10.1016/j.apcatb.2020.118722>.
  - [16] D.J. Deka, R. Daya, A. Ladshaw, D. Trandal, S.Y. Joshi, W.P. Partridge, Assessing impact of real-world aging on Cu-redox half cycles of a Cu-SSZ-13 SCR catalyst via transient response measurements and kinetic modeling, *Appl. Catal. B: Environ.* 309 (2022) 121233, <https://doi.org/10.1016/j.apcatb.2022.121233>.
  - [17] A. Guo, K. Xie, H. Lei, V. Rizzotto, L. Chen, M. Fu, P. Chen, Y. Peng, D. Ye, U. Simon, Inhibition effect of phosphorus poisoning on the dynamics and redox of Cu active sites in a Cu-SSZ-13 NH<sub>3</sub>-SCR catalyst for NO<sub>x</sub> reduction, *Environ. Sci. Technol.* 55 (2021) 12619–12629, <https://doi.org/10.1021/acs.est.1c03630>.
  - [18] F. Gao, D. Mei, Y. Wang, J. Szanyi, C.H.F. Peden, Selective catalytic reduction over Cu/SSZ-13: Linking homo- and heterogeneous catalysis, *J. Am. Chem. Soc.* 139 (2017) 4935–4942, <https://doi.org/10.1021/jacs.7b01128>.
  - [19] R. Daya, D. Trandal, R.K. Dadi, H. Li, S.Y. Joshi, J. Luo, A. Kumar, A. Yezerets, Kinetics and thermodynamics of ammonia solvation on ZrCu, ZrCuOH and ZrCu sites in Cu-SSZ-13 – Implications for hydrothermal aging, *Appl. Catal. B: Environ.* 297 (2021) 120444, <https://doi.org/10.1016/j.apcatb.2021.120444>.
  - [20] C. Paolucci, I. Khurana, A.A. Parekh, S. Li, A.J. Shih, H. Li, J.R.D. Iorio, J. D. Albarracin-Caballero, A. Yezerets, J.T. Miller, W.N. Delgass, F.H. Ribeiro, W. F. Schneider, R. Gounder, Dynamic multinuclear sites formed by mobilized copper ions in NO<sub>x</sub> selective catalytic reduction, *Science* 357 (2017) 898–903, <https://doi.org/10.1126/science.aan5630>.
  - [21] H. Lei, D. Chen, J.-y Yang, A. Khetan, J. Jiang, B. Peng, U. Simon, D. Ye, P. Chen, Revealing the formation and reactivity of cage-confined Cu pairs in catalytic NO<sub>x</sub> reduction over Cu-SSZ-13 zeolites by in situ UV–Vis spectroscopy and time-dependent DFT calculation, *Environ. Sci. Technol.* 57 (2023) 12465–12475, <https://doi.org/10.1021/acs.est.3c00458>.
  - [22] Y. Zhang, J. Zhang, H. Wang, W. Yang, C. Wang, Y. Peng, J. Chen, J. Li, F. Gao, Selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over Cu/SSZ-13: Elucidating dynamics of Cu active sites with in situ UV–Vis spectroscopy and DFT calculations, *J. Phys. Chem. C* 126 (2022) 8720–8733, <https://doi.org/10.1021/acs.jpcc.2c01268>.
  - [23] H. Lee, I. Song, S.W. Jeon, D.H. Kim, Mobility of Cu ions in Cu-SSZ-13 determines the reactivity of selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>, *J. Phys. Chem. Lett.* 12 (2021) 3210–3216, <https://doi.org/10.1021/acs.jpclett.1c00181>.
  - [24] N.D. Nasello, N. Usberti, U. Iacobone, F. Gramigni, W. Hu, S. Liu, I. Nova, X. Gao, E. Tronconi, Dual-site RHC and OHC transient kinetics predict Low-T standard SCR steady-state rates over a Cu-CHA catalyst, *ACS Catal.* 13 (2023) 2723–2734, <https://doi.org/10.1021/acscatal.2c06071>.
  - [25] W. Hu, T. Selli, F. Gramigni, E. Fenes, K.R. Rout, S. Liu, I. Nova, D. Chen, X. Gao, E. Tronconi, On the redox mechanism of Low-Temperature NH<sub>3</sub>-SCR over Cu-CHA: A combined experimental and theoretical study of the reduction half cycle, *Angew. Chem. Int. Ed.* 60 (2021) 7197–7204, <https://doi.org/10.1002/anie.202014926>.
  - [26] D. Chen, A. Khetan, H. Lei, V. Rizzotto, J.-Y. Yang, J. Jiang, Q. Sun, B. Peng, P. Chen, R. Palkovits, D. Ye, U. Simon, Copper site motion promotes catalytic NO<sub>x</sub> reduction under zeolite confinement, *Environ. Sci. Technol.* 57 (2023) 16121–16130, <https://doi.org/10.1021/acs.est.3c03422>.
  - [27] Y. Shen, T. Li, J. Yang, A. Wang, L. Wang, W. Zhan, Y. Guo, Y. Guo, Enhanced low-temperature performance of Al-rich Cu-SSZ-13 by Ce modification upon hydrothermal aging for NH<sub>3</sub>-SCR, *Chem. Eng. J.* 473 (2023) 145275, <https://doi.org/10.1016/j.cej.2023.145275>.
  - [28] Y. Shen, W. Dong, L. Zhang, L. Wang, B. Chen, Y. Guo, W. Zhan, A. Wang, C. Ge, Y. Guo, Revealing the mechanism of K-enhanced Cu-SSZ-13 catalysts against hydrothermal aging and P-poisoning for NO<sub>x</sub> reduction by NH<sub>3</sub>-SCR, *Sep. Purif. Technol.* 330 (2024) 125248, <https://doi.org/10.1016/j.seppur.2023.125248>.
  - [29] F. Gao, M. Kollár, R.K. Kukkadapu, N.M. Washton, Y. Wang, J. Szanyi, C.H. F. Peden, Fe/SSZ-13 as an NH<sub>3</sub>-SCR catalyst: a reaction kinetics and FTIR/Mössbauer spectroscopic study, *Appl. Catal. B: Environ.* 164 (2015) 407–419, <https://doi.org/10.1016/j.apcatb.2014.09.031>.
  - [30] E. Borfecchia, P. Beato, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga, Cu-CHA - a model system for applied selective redox catalysis, *Chem. Soc. Rev.* 47 (2018) 8097–8133, <https://doi.org/10.1039/c8cs00373d>.
  - [31] J. Hun Kwak, H. Zhu, J.H. Lee, C.H. Peden, J. Szanyi, Two different cationic positions in Cu-SSZ-13? *Chem. Commun.* 48 (2012) 4758–4760, <https://doi.org/10.1039/c2cc31184d>.
  - [32] R. Yu, Z. Zhao, S. Huang, W. Zhang, Cu-SSZ-13 zeolite-metal oxide hybrid catalysts with enhanced SO<sub>2</sub>-tolerance in the NH<sub>3</sub>-SCR of NO<sub>x</sub>, *Appl. Catal. B: Environ.* 269 (2020) 118825, <https://doi.org/10.1016/j.apcatb.2020.118825>.
  - [33] K.A. Tarach, M. Jabłońska, K. Pyra, M. Liebau, B. Reiprich, R. Gläser, K. Góra-Marek, Effect of zeolite topology on NH<sub>3</sub>-SCR activity and stability of Cu-exchanged zeolites, *Appl. Catal. B: Environ.* 284 (2021) 119752, <https://doi.org/10.1016/j.apcatb.2020.119752>.
  - [34] C. Fan, Z. Chen, L. Pang, S. Ming, C. Dong, K. Brou Albert, P. Liu, J. Wang, D. Zhu, H. Chen, T. Li, Steam and alkali resistant Cu-SSZ-13 catalyst for the selective catalytic reduction of NO<sub>x</sub> in diesel exhaust, *Chem. Eng. J.* 334 (2018) 344–354, <https://doi.org/10.1016/j.cej.2017.09.181>.
  - [35] J. Zhang, J. Liang, H. Peng, Y. Mi, P. Luo, H. Xu, M. He, P. Wu, Cost-effective fast-synthesis of chabazite zeolites for the reduction of NO<sub>x</sub>, *Appl. Catal. B: Environ.* 292 (2021) 120163, <https://doi.org/10.1016/j.apcatb.2021.120163>.
  - [36] Z. Chen, L. Liu, H. Qu, B. Zhou, H. Xie, Q. Zhong, Migration of cations and shell functionalization for Cu-Ce-La/SSZ-13@ZSM-5: the contribution to activity and hydrothermal stability in the selective catalytic reduction reaction, *J. Catal.* 392 (2020) 217–230, <https://doi.org/10.1016/j.jcat.2020.10.005>.
  - [37] L. Negahdar, N.E. Omori, M.G. Quesne, M.D. Frogley, F. Cacho-Nerin, W. Jones, S. W.T. Price, C.R.A. Catlow, A.M. Beale, Elucidating the significance of copper and nitrate speciation in Cu-SSZ-13 for N<sub>2</sub>O formation during NH<sub>3</sub>-SCR, *ACS Catal.* 11 (2021) 13091–13101, <https://doi.org/10.1021/acscatal.1c03174>.
  - [38] H. Jiang, B. Guan, H. Lin, Z. Huang, Cu/SSZ-13 zeolites prepared by in situ hydrothermal synthesis method as NH<sub>3</sub>-SCR catalysts: influence of the Si/Al ratio on the activity and hydrothermal properties, *Fuel* 255 (2019) 115587, <https://doi.org/10.1016/j.fuel.2019.05.170>.
  - [39] A. Wang, M. Elena Azzoni, J. Han, K. Xie, L. Olsson, Insight into the effect of phosphorus poisoning of Cu/zeolites with different framework towards NH<sub>3</sub>-SCR, *Chem. Eng. J.* 454 (2023) 140040, <https://doi.org/10.1016/j.cej.2022.140040>.
  - [40] B. Mozgawa, F. Zasada, M. Fedyna, K. Góra-Marek, E. Tabor, K. Mlekodaj, J. Dedecek, Z. Zhao, P. Pietrzyk, Z. Sojka, Analysis of NH<sub>3</sub>-TPD profiles for CuSSZ-13 SCR catalyst of controlled Al distribution - complexity resolved by first principles thermodynamics of NH<sub>3</sub> desorption, IR and EPR insight into Cu speciation, *Chem. - A Eur. J.* 27 (2021) 17159–17180, <https://doi.org/10.1002/chem.202102790>.
  - [41] Q. Xu, Z. Fang, Y. Chen, Y. Guo, Y. Guo, L. Wang, Y. Wang, J. Zhang, W. Zhan, Titania-samarium-manganese composite oxide for the low-temperature selective catalytic reduction of NO with NH<sub>3</sub>, *Environ. Sci. Technol.* 54 (2020) 2530–2538, <https://doi.org/10.1021/acs.est.9b06701>.
  - [42] L. Ma, Y. Cheng, G. Cavataio, R.W. McCabe, L. Fu, J. Li, Characterization of commercial Cu-SSZ-13 and Cu-FAPO-34 catalysts with hydrothermal treatment for NH<sub>3</sub>-SCR of NO<sub>x</sub> in diesel exhaust, *Chem. Eng. J.* 225 (2013) 323–330, <https://doi.org/10.1016/j.cej.2013.03.078>.
  - [43] F. Gao, E.D. Walter, E.M. Karp, J. Luo, R.G. Tonkyn, J.H. Kwak, J. Szanyi, C.H. F. Peden, Structure–activity relationships in NH<sub>3</sub>-SCR over Cu-SSZ-13 as probed by reaction kinetics and EPR studies, *J. Catal.* 300 (2013) 20–29, <https://doi.org/10.1016/j.jcat.2012.12.020>.
  - [44] F. Gao, E.D. Walter, M. Kollár, Y. Wang, J. Szanyi, C.H.F. Peden, Understanding ammonia selective catalytic reduction kinetics over Cu/SSZ-13 from motion of the Cu ions, *J. Catal.* 319 (2014) 1–14, <https://doi.org/10.1016/j.jcat.2014.08.010>.
  - [45] W. Su, H. Chang, Y. Peng, C. Zhang, J. Li, Reaction pathway investigation on the selective catalytic reduction of NO with NH<sub>3</sub> over Cu/SSZ-13 at low temperatures, *Environ. Sci. Technol.* 49 (2015) 467–473, <https://doi.org/10.1021/es503430w>.

- [46] B. Jiang, S. Zhao, Y. Wang, Y. Wenren, Z. Zhu, J. Harding, X. Zhang, X. Tu, X. Zhang, Plasma-enhanced low temperature  $\text{NH}_3$ -SCR of  $\text{NO}_x$  over a Cu-Mn/SAPO-34 catalyst under oxygen-rich conditions, *Appl. Catal. B: Environ.* 286 (2021) 119886, <https://doi.org/10.1016/j.apcatb.2021.119886>.
- [47] A. Wang, L. Olsson, Insight into the  $\text{SO}_2$  poisoning mechanism for  $\text{NO}_x$  removal by  $\text{NH}_3$ -SCR over Cu/LTA and Cu/SSZ-13, *Chem. Eng. J.* 395 (2020) 125048, <https://doi.org/10.1016/j.cej.2020.125048>.
- [48] C. Negri, T. Selli, E. Borfecchia, A. Martini, K.A. Lomachenko, T.V.W. Janssens, M. Cutini, S. Bordiga, G. Berlier, Structure and reactivity of oxygen-bridged diamino dicopper(II) complexes in Cu-ion-exchanged chabazite catalyst for  $\text{NH}_3$ -mediated selective catalytic reduction, *J. Am. Chem. Soc.* 142 (2020) 15884–15896, <https://doi.org/10.1021/jacs.0c06270>.
- [49] Y. Xin, Q. Li, Z. Zhang, Zeolitic materials for  $\text{DeNO}_x$  selective catalytic reduction, *ChemCatChem* 10 (2018) 29–41, <https://doi.org/10.1002/cctc.201700854>.